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(54) Title: DRY BATTERY HAVING A CATHODE WITH ADDITIVES

(57) Abstract

The battery is of the primary alkaline type and comprises a zinc anode, an anodic gel and a cathode comprising a depolarizing mixture based on manganese dioxide containing rutile, an allotropic form of titanium dioxide.

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Dry battery having a cathode with additives

DESCRIPTION

Technical Field

The present invention relates to a dry battery having a cathode with additives, and more particularly, to a dry battery of the primary alkaline type.

Background of the Invention

It is known to use anatase, an allotropic form of titanium dioxide, as an additive to the manganese dioxide commonly used in the cathode of primary and secondary dry alkaline batteries in order to obtain a longer service life in uses with high current consumption such as, for example, in flash cameras and for powering toys. Such a use of anatase is, for example, cited in US Patent 5,342,712, wherein, for the formation of the cathodic mixture, anatase, manganese dioxide and graphite are mixed. Such a mixture is compacted into the form of small cylinders perforated in the centre so they can be superposed in a suitable number in a small iron tube in order to form a battery and, for completion of the latter, further phases follow according to a known process.

Such a battery with anatase as cathodic additive permits, in uses with high current consumption, an increase in service life which can be as much as 15% as compared with an analogous battery without additive. On the other hand, in uses with low current consumption, the service life of the battery with additive is diminished, again by up to 15%. This behaviour makes the batteries provided with an additive in this way particularly suitable for supplying a photographic flash bulb, and in general wherever high intensity-discharges are required, guaranteeing in such cases a longer service life compared

with conventional batteries.

For a given battery volume, the quantity of anatase used will diminish the quantity of manganese dioxide or of active material of the cathode; in the cited document, the advantage found is attributed to a higher ion mobility during the discharge, which higher mobility would have been caused by the presence of the anatase. It is nevertheless clear that such an effect cannot be enhanced beyond a certain limit by increasing the quantity of anatase, because beyond such a limit the negative effect of the reduction of the quantity of manganese dioxide, which constitutes the active part of the cathode, prevails. For this reason, the maximum quantity of anatase used in practice is 5%.

Objects and Summary of the Invention

The object of the present invention is a further improvement in the performance of a battery with an additive, which gives higher efficiency per unit volume relative to anatase. Rutile, another allotropic form of titanium oxide, which has a density 10% higher than that of anatase, has been identified as such an additive. It has been proved that the use of rutile as additive in a dry battery is, under certain conditions, more effective than anatase in increasing the discharge duration of a battery at higher voltages. Moreover, rutile has a higher density than anatase and therefore, if added to the mixture for forming the cathode in an equal percentage quantity by weight (as compared with anatase), allows the use in the same total volume of the cathodic mass of a greater quantity of manganese dioxide, with the advantage of permitting a longer discharge duration at all voltages, as compared with that of a battery with anatase as additive.

Brief Description of the Drawings

The invention will be better understood by following the description and the attached drawing which refers to properties useful in the evaluation of the inventive content of the invention. In the drawing:
Figures 1 to 9 show graphs of the discharge of batteries with additives, respectively, of anatase and rutile in comparison with each other and with batteries without additives.

Detailed Description

For the comparison of the efficiency of the additives, tests under various discharge conditions were carried out, both intermittently and continuously and with loads of various magnitude (expressed by the electrical resistance in ohm). The results of these tests are reported below; for these tests, batteries comprising a zinc anode, an anodic gel containing caustic potash, a corrosion inhibitor without addition of mercury and a cathode, containing a depolarizing mixture based on manganese dioxide and graphite were prepared. For all the batteries, the same constructional criterion was used and the same common components were utilized, in order to guarantee the utmost uniformity in the batteries themselves which were produced from a single batch of common material. The test was carried out with a uniform criterion with respect also to the ageing of the batteries, namely the time elapsed from the formation of each battery and the test itself.

For the batteries with additives, the quantity of additive is indicated in terms of per cent by weight relative to the mixture which makes up the cathode before the addition of the alkaline part.

In the figures, along the ordinate axis, the discharges of batteries without additive are marked 1, the discharges of batteries with 1% of anatase additive are

marked 2 and the discharges of batteries with 1% of rutile additive are marked 3. On the abscissa, the durations are indicated by the number of cycles, for the tests with intermittent discharges of short duration (of the order of a few seconds) or by hours of effective discharge for the tests with intermittent discharges of longer duration (of the order of an hour) or continuous discharge. For each test, the result assumed is, respectively, the number of complete discharge cycles or the number of hours of effective discharge elapsed until the potential of the battery has fallen to the value E.P. (end point) shown on each figure, in accordance with the standard IEC 86/1. For each type of battery, the right-hand border of the hatched area represents in the figures the average of the values obtained with further successive tests.

Figure 2 refers to tests of intermittent discharge with repetition of cycles of 15 second-discharges every minute with a load of 1.8 ohm. Under such discharge conditions, the batteries with additives all have a longer service life than the batteries without additive. In particular, this advantage is greatest for the rutile, a service life 22% greater than for batteries without additive and 10% greater relative to batteries with anatase additive having been obtained.

Figures 4 to 6 give the results of intermittent discharge tests of one hour on each consecutive day. Under these conditions, the use of the additives was shown to have no advantages at loads of 10 and 40 ohm (Figures 5 and 6) but to be advantageous at lower loads. For example, at a load of 3.9 ohm (Figure 4), the batteries with anatase showed a service life 21% higher than those without additives, the batteries with rutile giving a slightly less advantageous result with terminal 0.9V.

In Figures 1, 3 and 7 to 9, results of tests with continuous discharges are reported. Under these conditions, the batteries with additives show an advantage

of about 22% at a load of 1.5 ohm (Figure 1), with equal performances by rutile and anatase, an advantage of 26% for batteries with rutile and 18% for batteries with anatase at a load of 3.9 ohm (Figure 3) and of about 24% for both the additives at 6.8 ohm (Figure 9), whereas the period is virtually the same for all the types of battery at loads greater than 10 ohm.

The tests illustrated above, although they confirm the general effectiveness of the titanium oxide additives in increasing the discharge duration at low loads - and therefore at high current consumptions - showed that, in particular for uses with flash in cameras, where short discharges of high current intensity with high voltages are required (Figure 2), the rutile at equal content in per cent by weight shows a consistent advantage over anatase, which advantage is reduced down to vanishing point and becomes negative in the applications where the consumption is low and where the admissible end voltage falls to below 0.9V.

Under the conditions of continuous discharge, the batteries with rutile proved to have a service life longer than or equal to that of the batteries with anatase (and thus longer than that of the batteries without additives) for discharges up to 6.8 ohm (Figures 1, 3 and 7).

Moreover, since the density of rutile is about 10% higher than that of anatase, these advantages can be further enhanced because, with the same quantity of manganese dioxide, it is possible to use, in the same volume of battery, either a larger quantity of additive or a larger quantity of manganese dioxide, or a combination of both these measures.

The drawing is only intended to show an embodiment, given solely as a demonstration of the invention in practice, and this invention can vary in forms and arrangements without otherwise departing from the scope of the concept forming the invention itself.

Where reference numbers are given in the attached claims, they are intended to facilitate reading of the claims with reference to the description and to the drawing, without limiting the scope of the protection represented by the claims.

CLAIMS

1. Dry battery of the primary alkaline type, including: a zinc anode, an anodic gel containing an alkaline compound; and a cathode containing a depolarizing mixture based on manganese dioxide and graphite, characterized in that said mixture contains rutile, an allotropic form of titanium dioxide.

2. Battery according to Claim 1, characterized in that the rutile is present in said mixture in a percentage quantity of between 0.1 and 5%.

3. Battery according to Claim 2, characterized in that said percentage quantity is 1%.

4. Battery according to one or more of the preceding claims, characterized in that said anode contains corrosion inhibitors and/or a mercury amalgam.

5. Battery according to one or more of the preceding claims, characterized in that said alkaline compound is caustic potash or magnesium hydroxide or the like.

6. Dry battery and manufacturing process therefor, all as described above.

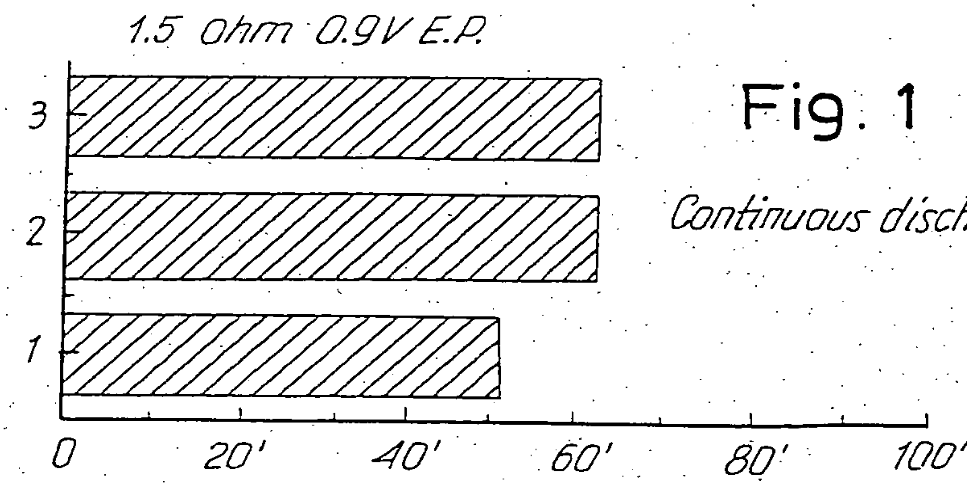

Fig. 1

Continuous discharge

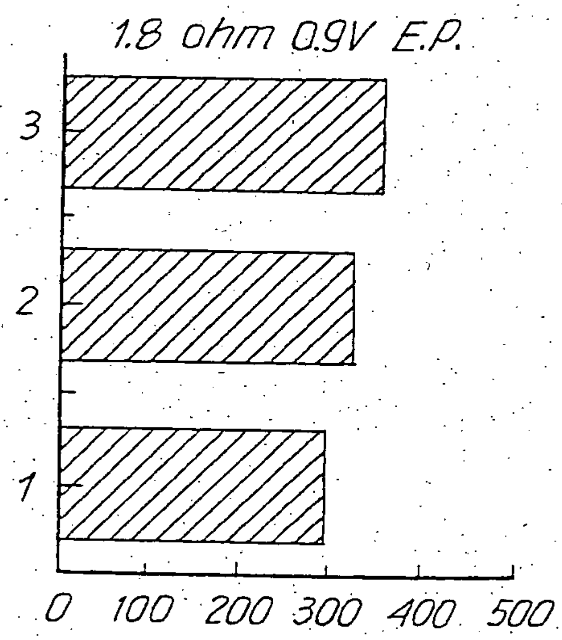

Fig. 2

Test according to standard IEC 86/1

Intermittent discharge (15"/1)

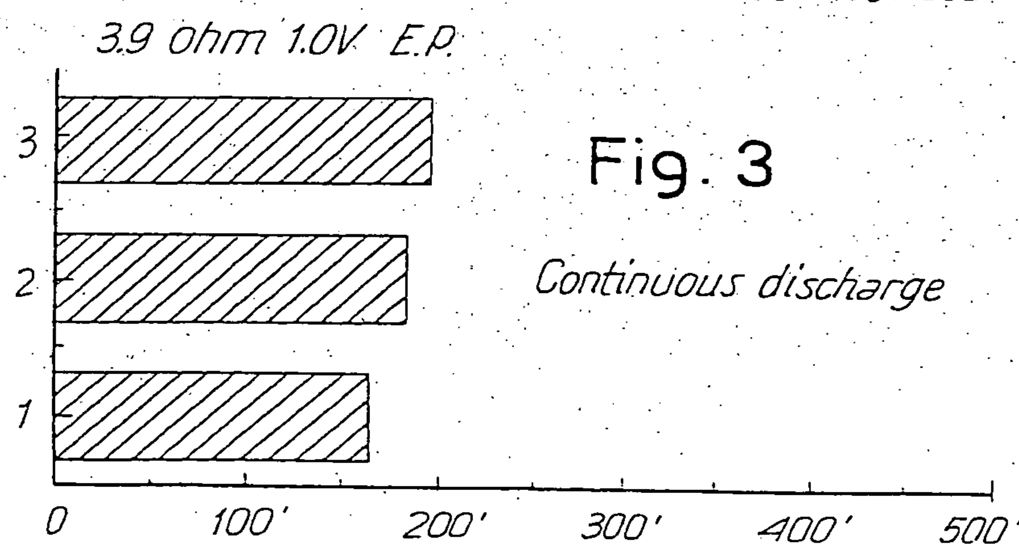

Fig. 3

Continuous discharge

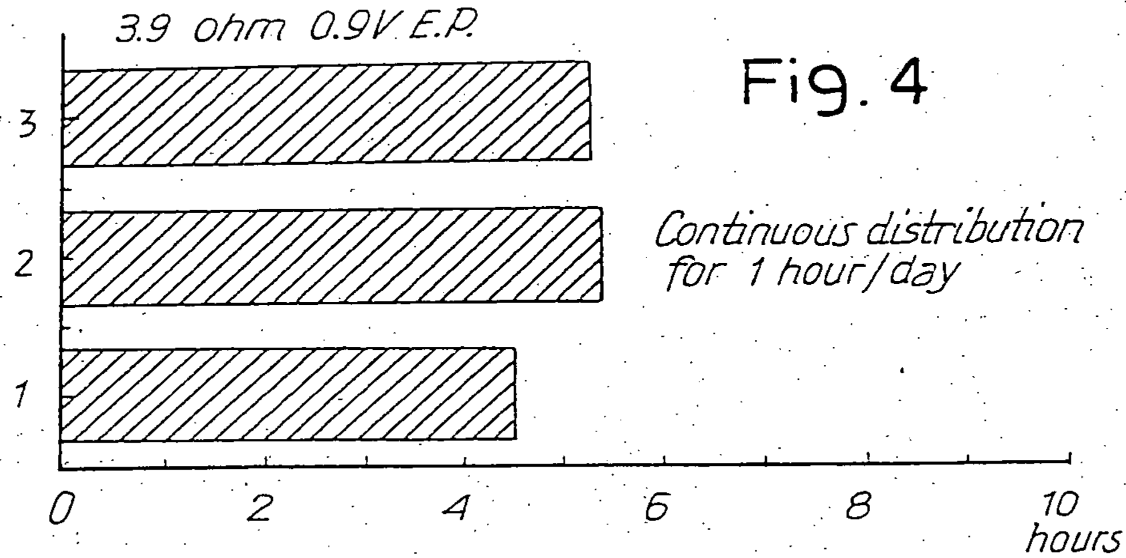

Fig. 4

Continuous distribution
for 1 hour/day

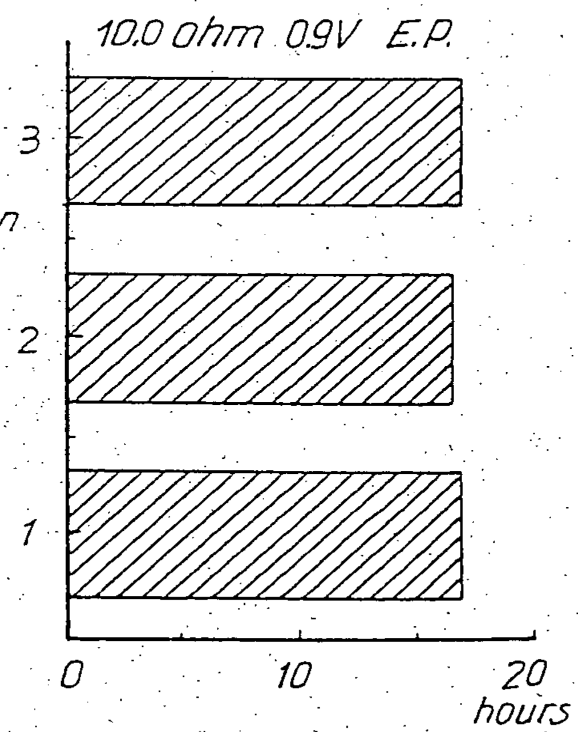

Fig. 5

Continuous distribution
for 1 hour/day

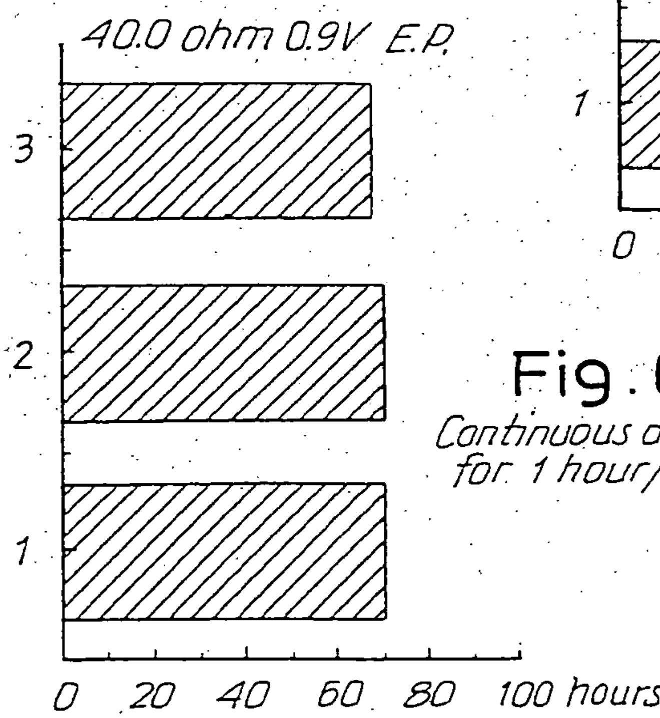

Fig. 6

Continuous distribution
for 1 hour/day

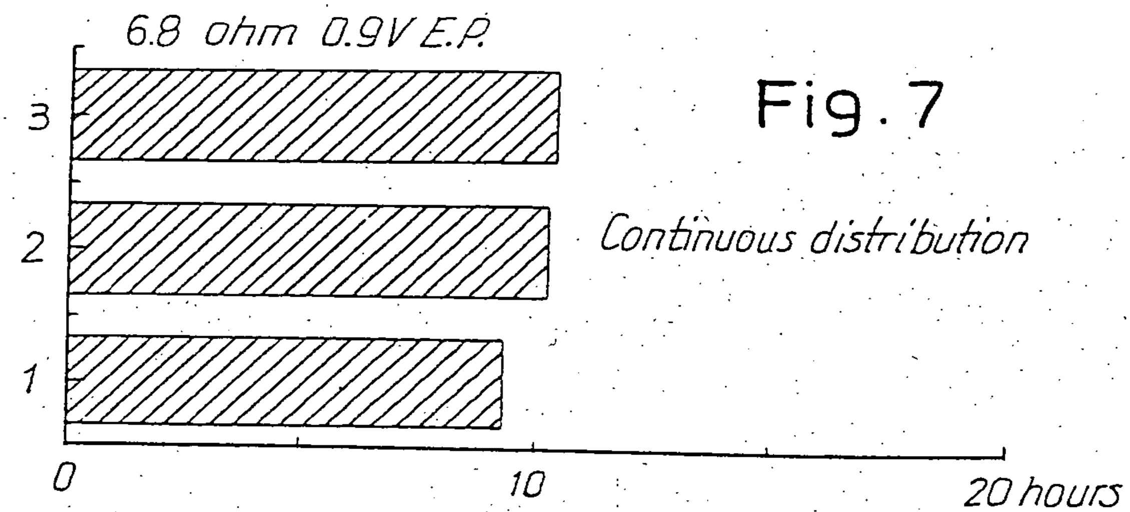

Fig. 7

Continuous distribution

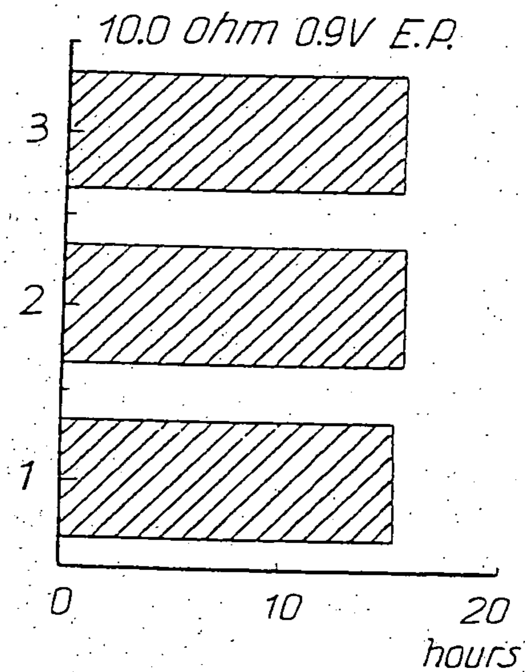

Fig. 8

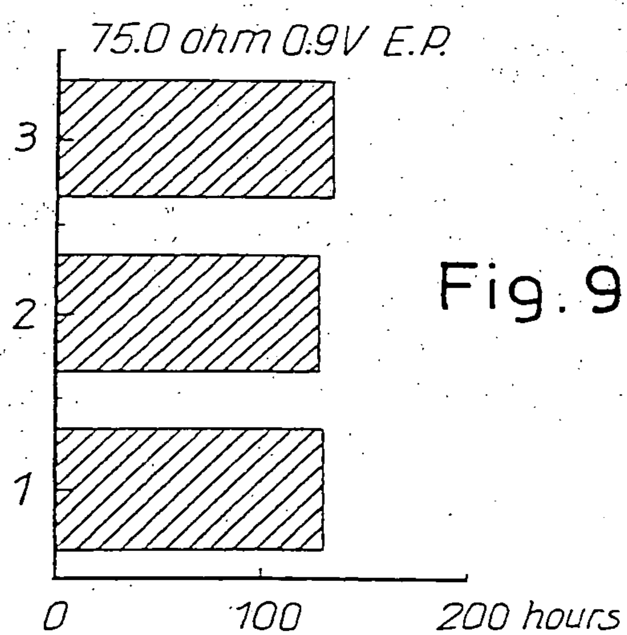

Fig. 9

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IT 96/00103

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M4/50 H01M4/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,5 342 712 (JOLA E. MIECZKOWSKA) 30 August 1994 cited in the application see column 2, line 39-50 ---	1,2
Y	DE,A,33 37 568 (VARTA BATTERIE AG) 25 April 1985 see page 7, line 30 - page 8, line 1 ---	1,2
A	US,A,4 549 943 (GEOFFREY W. MELLORS) 29 October 1985 see column 3, line 34 - column 5, line 42 ---	1-6

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
28 August 1996	13.09.96

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 355 (E-661), 22 September 1988 & JP,A,63 110547 (MITSUBISHI PAPER MILLS LTD) see abstract ---	1
A	EP,A,0 383 161 (KOSAKA CORPORATION) 22 August 1990 see page 11, line 1 - page 12; table 3 see claims 1-7 -----	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IT 96/00103

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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